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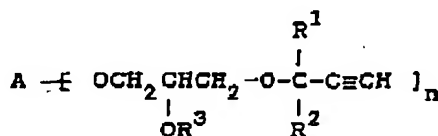
(71) Applicant: NIPPON PAINT CO., LTD.
1-2, Oyodokita 2-chome Kita-ku
Osaka-shi(JP)

(72) Inventor: Yamada, Mitsuo
B-714, 46 Yamadaminami
Suite, Osaka-fu(JP)
Inventor: Aoki, Kei
1-16-7 Shikanodai nishi
Ikoma, Nara-ken(JP)
Inventor: Mizuguchi, Ryuzo
42-6-301 Hashimoto Kurigatani
Yawata, Kyoto-fu(JP)

(73) Representative: Kinzobach, Werner, Dr. et al
Patentanwälte Reitschler, Kinzobach und
Partner Sternwartstrasse 4 Postfach 86 06 49
W-8000 München 86(DE)

(54) Modified epoxy resins having acetylenically unsaturated functions.

(57) A modified epoxy resin or compound of the formula:



wherein A is the backbone residue of a glycidyl ether or ester type epoxy resin with removal of the glycidyloxy groups; R¹ and R² are independently a hydrogen atom or C₁-C₁₂ alkyl; R³ is a hydrogen atom or a glycidyl group; and n is an integer of greater than 1. A method for producing the modified epoxy resin is also disclosed.

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Background of the Invention

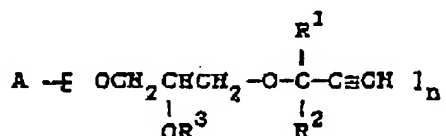
This invention relates to modified epoxy resins or compounds having acetylenically unsaturated functions. These resins or compounds may be used in a nonemanating resinous composition capable of curing through different curing mechanisms appropriate to the different functional groups.

It has been known that certain compounds having acetylenically unsaturated groups such as ethynyl or propynyl group may be polymerized into a conjugated diene polymer. Because of their unique polymerization mechanism and the unique electrical and physical properties of their polymers, such compounds are attracting a great interest as a component for producing self-curable, nonemanating resinous compositions. Japanese Patent Kokai No. 108213/88, for example, discloses a propargyl ether of cresol novolac resin as one of such compounds.

The present invention provides a novel class of epoxy-based modified resins having a plurality of acetylenically unsaturated functions in the molecule.

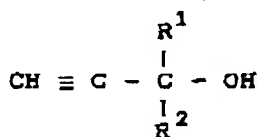
Summary of the Invention

According to one aspect of the present invention, there is provided a resin or compound having the formula:

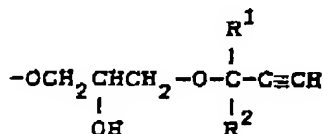


wherein, A is the backbone residue of a glycidyl ether or ester type epoxy resin or compound with removal of the terminal glycidyloxy groups, R¹ and R² are independently hydrogen atom or C₁-C₁₂ alkyl, R³ is a hydrogen atom or glycidyl group, and n is an integer of greater than 1.

According to another aspect of the present invention, there is provided a method for modifying a glycidyl ether or ester type epoxy resin or compound which comprises reacting a resin or compound having a plurality of terminal glycidyloxy groups with an acetylenic alcohol of the formula:



wherein R¹ and R² are as defined, to obtain a corresponding resin or compound having a plurality of terminal groups of the formula:

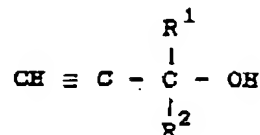


wherein R¹ and R² are as defined.

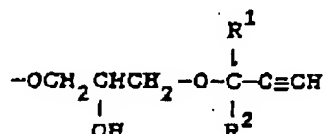
According to a further aspect of the present invention, there is provided a method for modifying a glycidyl ether or ester type epoxy resin or compound which comprises the steps of:

(a) reacting a resin or compound having a plurality of terminal glycidyloxy groups with an acetylenic alcohol of the formula:

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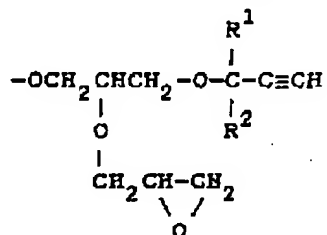


wherein R¹ and R² are as defined, to obtain a corresponding resin or compound having a plurality of terminal groups of the formula:



wherein R¹ and R² are as defined;

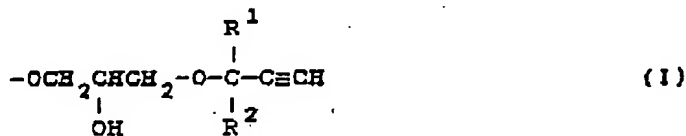
(b) reacting the product of step (a) with epichlorohydrin or glycerol-1,3-dichlorohydrine and then with an alkali to obtain a corresponding resin or compound having a plurality of terminal groups of the formula:



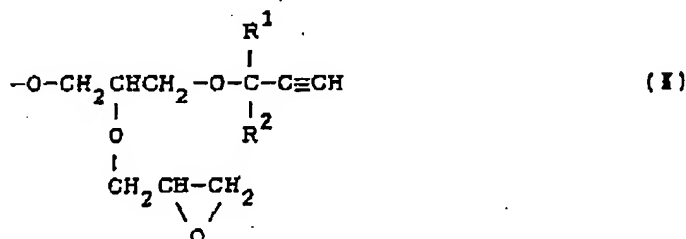
wherein R¹ and R² are as defined.

35 Detailed Discussion

The resin or compound of the present invention is characterized by possessing a plurality of terminal groups of the formula:



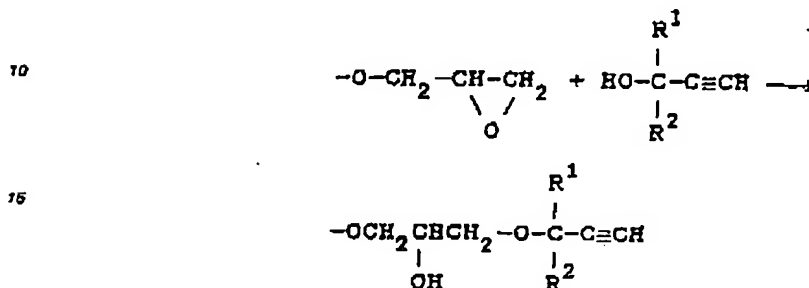
or,



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instead of terminal glycidyloxy groups possessed by convention epoxy resins or compounds.

Starting from such conventional epoxy resins or compounds, the overall steps for obtaining the desired products include the following reactions:

5 Step (a)

Typical starting materials which may be used herein include bisphenol type epoxy resins such as bisphenol A epoxy resin, bisphenol S epoxy resin, bisphenol F epoxy resin and halogen-substituted bisphenol epoxy resin. The term "bisphenol" as used herein include those compounds in which two phenolic molecules are coupled together by a bridge such as direct bond, $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CF}_3)_2-$, $-\text{O}-$, $-\text{CO}-$, $-\text{S}-$, $-\text{SO}_2-$ and the like. Bisphenol epoxy resins are produced, as is well-known, by reacting bisphenols with epichlorohydrine in the presence of an alkali. Diglycidyl ethers of bisphenols are preferably used.

Novolac epoxy resin may also be used as well.

Another class of epoxy resins or compounds comprises diglycidyl ethers of glycols such as 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, hydrogenated bisphenol A, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, alkylene oxide-adducts of bisphenols and the like.

A further class of epoxy resins or compounds comprises diglycidyl esters of dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, hexahydrophthalic acid, 4-methylhexahydrophthalic acid, tetrahydrophthalic acid, phthalic acid, isophthalic acid, terephthalic acid and the like.

Acetylenic alcohols used in step (a) include propargyl alcohol and its α -mono- and α,α -di- C_1 - C_{12} , preferably C_1 - C_4 alkyl derivatives. Propargyl alcohol is preferred.

The reaction may be carried out in the presence of a basic catalyst such as tertiary amines, quaternary ammonium salts or alkali metal hydroxides either in an inert solvent or without using the solvent. An excess of acetylenic alcohol may be used as a diluent. A reaction temperature ranging between 80°C and 180°C may be employed.

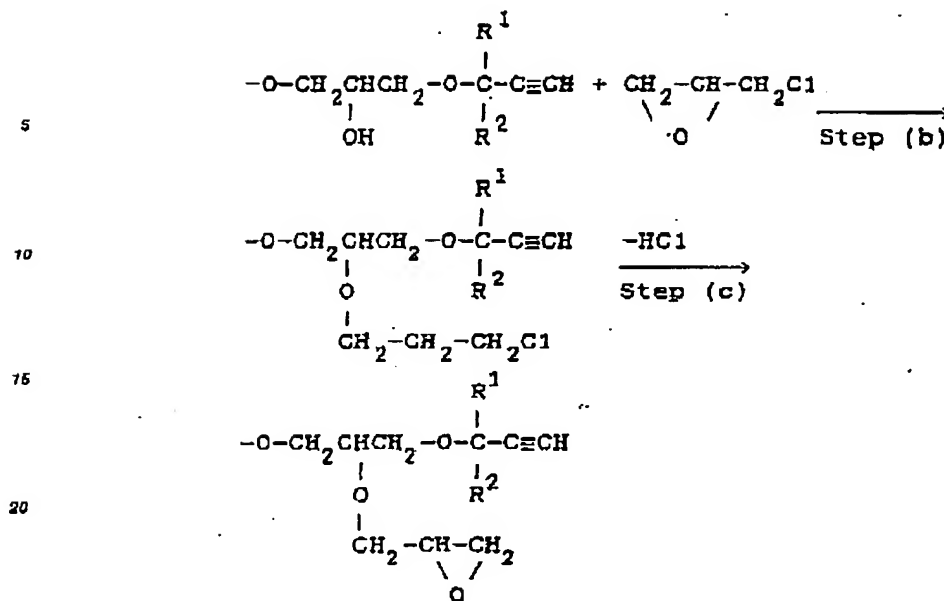
The reaction product may be purified by the conventional technique such as fractional distillation and used as a component of nonemulating resinous compositions, or they may be subjected to the steps (b) and (c) below to introduce an epoxy function.

45 Steps (b) and (c)

50

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Steps (b) and (c) may be performed either sequentially or simultaneously.

In the sequential process, the product of step (a) is reacted with epichlorohydrin or glycerol-1,3-dichlorohydrin in the presence of a Lewis acid catalyst such as boron trifluoride or its complex, stannic chloride and the like and then with an alkali such as sodium hydroxide, sodium carbonate, barium hydroxide and the like. It is preferable to use epichlorohydrin or glycerol-1,3-dichlorohydrin in excess, for example, about 1.5 to times on the equivalent basis.

In the simultaneous process, the product of step (a) is reacted with an excess of epichlorohydrin in the presence of an alkali such as sodium hydroxide and a phase transfer catalyst or tertiary amine or quaternary ammonium base. Typical examples of phase transfer catalyst include methyltriocetylammmonium chloride, methyltridecylammmonium chloride, tetramethylammmonium chloride and tetrabutylammmonium bromide, and examples of quaternary ammonium base include benzyltrimethylammmonium hydroxide.

An excess, for example, about 2.5 to about 10 times on the equivalent basis of epichlorohydrin serves to absorb hydrogen chloride produced as a reaction by-product and is converted into glycerol-1,3-dichlorohydrin.

In the both processes, the reaction may be carried out in an inert solvent such as hydrocarbon solvents, ethers and ketones at a temperature from 40 °C to the boiling point of the solvent used.

After removing the solvent, the reaction product may be purified by the conventional technique although crude products containing a small amount of by-products such as chlorohydrin ethers produced in step (b) or hydrolysate of the product of step (c) may be tolerated.

The resins or compounds thus prepared may be polymerized with a metallic catalyst or initiator, or by irradiating with actinic radiations such as UV radiation, gamma radiation or electron beam radiation. They are, therefore, useful as stock materials of resins used in paints, electric and electronic components, structural materials and nonlinear optical materials where nonemitting cure is desired in the finished products.

The invention is illustrated by the following examples wherein all parts and percents are by weight unless otherwise specified.

Example 1

A flask equipped with a stirrer, thermometer, nitrogen gas tube and reflux condenser was charged with 475 g of a bisphenol A epoxy resin having an epoxy equivalent of 170, 280 g of propargyl alcohol and 3.075 g of tetrabutylammmonium chloride. The mixture was allowed to react by heating at 120 °C until the epoxy

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equivalent measured by the HCl-dioxane titration method was greater than 15,000. After the reaction, the product was evaporated in vacuo to remove unreacted propargyl alcohol and then poured in 3 liter of methanol with stirring. After standing at room temperature methanol was removed to give a viscous resin having a number average molecular weight as determined by the GPC method of 500.

5 The structure of the product was identified by the IR spectrum and ¹H-NMR.

IR: 3300 cm⁻¹, 2100 cm⁻¹ (CH≡C-); 1610 cm⁻¹,

1510 cm⁻¹ (Phe); 1110 cm⁻¹ (-O-).

¹H-NMR (δ, ppm): 2.5 (-C≡CH).

10 Example 2

A flask as used in Example 1 was charged with 500 g of a bisphenol A epoxy resin having an epoxy equivalent of 450, 139 g of polycaprolactone polyol having a number average molecular weight of 500, 3.18 g of benzyldimethylamine and 180 g of xylene. The mixture was allowed to react by heating at 150 °C until an epoxy equivalent of 1200 was reached.

15 After the above chain-extending reaction, the product was further reacted with 80 g of propargyl alcohol until the epoxy function disappeared. The reaction mixture was then evaporated in vacuo to remove unreacted propargyl alcohol and xylene, and poured in 3 liter of methanol with stirring. After standing at room temperature, methanol was removed to give a viscous resin having a number average molecular weight of 2600 as determined by the GPC method.

20 IR: 3300 cm⁻¹, 2100 cm⁻¹ (CH≡C-), 1110 cm⁻¹ (-O-).

¹H-NMR (δ, ppm): 2.5 (-C≡CH).

Example 3

25 Analogous to Example 1, 475 g of 1,4-diglycidyloxybutane was reacted with 528 g of propargyl alcohol to give 1,4-bis(3-propargyloxy-2-hydroxypropyl) oxybutane.

IR: 3300 cm⁻¹, 2100 cm⁻¹ (CH≡C-).

¹H-NMR (δ, ppm): 2.5 (-C≡CH).

30 Example 4

Analogous to Example 1, 475 g of a cresol novolac epoxy resin having an epoxy equivalent of 220 (Toto Kasel K.K., YDCN-704) was reacted with 240 g of propargyl alcohol. A resin having a number average

35 molecular weight of 2500 was obtained.

IR: 3300 cm⁻¹, 2100 cm⁻¹ (CH≡C-), 1110 cm⁻¹ (-O-).

¹H-NMR (δ, ppm): 2.5 (-C≡CH).

Example 5

40 Analogous to Example 1, 475 g of a bisphenol A epoxy resin having an epoxy equivalent of 450 was reacted with 180 g of 2-methyl-3-butyne-2-ol to give a resin having a number average molecular weight of 1200.

IR: 3300 cm⁻¹, 2100 cm⁻¹ (CH≡C-), 1110 cm⁻¹ (-O-).

45 ¹H-NMR (δ, ppm): 2.5 (-C≡CH).

Example 6

2,2-Bis[4-(3-propargyloxy-2-glycidyloxypropyloxy)-phenyl]propane

50 A flask equipped with a stirrer, thermometer, nitrogen gas tube and reflux condenser was charged with 170.0 g of bis(4-glycidyloxyphenyl)propane, 224.0 g of propargyl alcohol and 1.0 g of benzyldimethylamine. The mixture was allowed to react by heating at 115 °C until no epoxide function was detected by the HCl-dioxane titration method. After the reaction, unreacted propargyl alcohol was removed from the reaction mixture by evaporation in vacuo.

To the mixture were added 740.0 g of epichlorohydrine and 4.0 g of tetramethylammonium chloride. To the mixture heated at 50 °C, 86.0 g of 50 % aqueous solution of sodium hydroxide was added dropwise over 2 hours. Then reaction was continued for additional 4 hours while removing water as an azeotropic

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mixture with epichlorohydrine in vacuo. After removing excessive epichlorohydrine, the reaction product was treated with toluene-water mixture to extract sodium chloride by-product in water and the toluene fraction was evaporated in vacuo to remove the solvent. The title compound having an epoxy equivalent of 280 (283 in theory) was obtained in a yield of 80.0 % of theory.

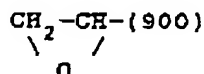
5 IR (cm⁻¹) :

CH₂=C-(3300, 2100)

CH₂-(2900)

-Ph-(1600, 1500)

10

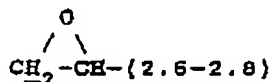


15 ¹H-NMR (ppm) :

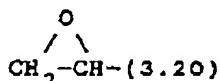
CH₃-(1.62)

CH₂=C-(2.44)

20



25



=C-CH₂-(4.18)

30 Ph-H(6.80-7.13)

Example 7

Bis(4-(3-propargyloxy-2-glycidyloxypropyloxy)-phenyl)methane

35

A flask as used in Example 6 was charged with 155.0 g of bis(4-glycidyloxyphenyl)methane, 224.0 g of propargyl alcohol and 1.0 g of tetramethylammonium chloride. The mixture was allowed to react by heating at 115 °C until no epoxide function was detected by the HCl-dioxane titration method. After the reaction, unreacted propargyl alcohol was removed from the reaction mixture by evaporation in vacuo.

40 To the mixture was added 0.5 g of boron trifluoride-diethyl ether complex and the temperature raised to 80 °C. To this was added dropwise 103.0 g of epichlorohydrine and the reaction was continued until the epoxide function disappeared. Then 160.0 g of 50 % aqueous solution of sodium hydroxide was added to the cooled reaction mixture and allowed to react for additional 6 hours at 30 °C. After the reaction, excessive sodium hydroxide was neutralized and the product was washed with deionized water repeatedly to remove sodium chloride by-product. The title compound having an epoxy equivalent of 280 was obtained in a yield of 80.0 % of theory.

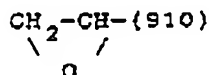
45

IR (cm⁻¹) :

CH₂=C-(3300, 2100)

-Ph-(1600, 1510)

50

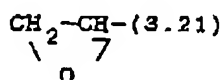
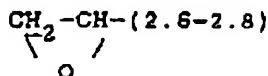


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¹H-NMR (ppm) :

CH₂=C-(2.46)

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10 $\equiv\text{C}-\text{CH}_2-(4.19)$
Ph-H(6.81-7.15)

Example 8

15 Bis[4-(3-propargyloxy-2-glycidyloxypropyloxy)-phenyl]sulfone

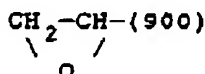
A flask as used in Example 6 was charged with 180.0 g of bis(4-glycidyloxyphenyl)sulfone, 224.0 g of propargyl alcohol and 1.0 g of tetramethylammonium chloride. The mixture was allowed to react by heating at 115 °C until no epoxide function was detected by the HC1-dioxane titration method. After the reaction
20 unreacted propargyl alcohol was removed from the reaction mixture by evaporation in vacuo.

To the mixture were added 40.0 g of epichlorohydrine and 4.0 g of tetramethylammonium chloride. To the mixture heated at 50 °C, 88.0 g of 50 % aqueous solution of sodium hydroxide was added dropwise over 2 hours. Then reaction was continued for additional 4 hours while removing water as an azeotropic mixture with epichlorohydrine in vacuo. After removing excessive epichlorohydrine, the reaction product was
25 treated with toluene-water mixture to extract sodium chloride by-product in water and the toluene fraction was evaporated in vacuo to remove the solvent.

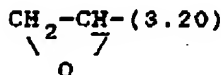
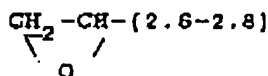
The title compound having an epoxy equivalent of 300 was obtained in a yield of 92.0 % of theory.

IR (cm⁻¹):

CH=CH-(3300, 2100)



35 H-NMR (ppm)
CH=CH-(2.44)



$\equiv\text{C}-\text{CH}_2-(4.19)$
Ph-H(6.80-7.14)

60 Analogous to Example 6, the following compounds were produced.

Example 9

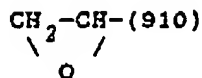
4,4'-Bis(3-propargyloxy-2-glycidyloxypropyloxy)-benzophenone

65 Epoxy equivalent : 278
Yield : 92.4 %
IR (cm⁻¹):

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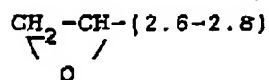
CH=C-(3300, 2100)
-Ph-(1600, 1500)

5



H-NMR (ppm) :
CH=C-(2.45)

10



15

Ph-H(6.6-7.8)

Example 10

20

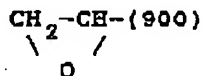
4,4'-Bis(3-propargyloxy-2-glycidyloxypropyloxy)-biphenyl

Epoxy equivalent : 268
Yield : 86.5 %

IR (cm⁻¹) :
CH=C-(3300, 2100)
-Ph-(1600, 1500)

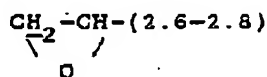
25

30



H-NMR (ppm) :
CH=C-(2.45)

35



40

Ph-H(6.6-7.8)

Example 11

45

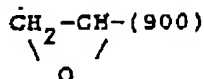
2,2-Bis(4-(3-propargyloxy-2-glycidyloxypropyloxy)-2-methylphenyl)propane

Epoxy equivalent : 312
Yield : 88.3 %

IR (cm⁻¹) :
CH=C-(3300, 2100)
-Ph-(1600, 1500)

50

55



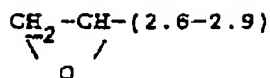
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H-NMR (ppm) :

-CH₂-(1.70)

CH=C-(2.44)

5



10 Ph-H(6.6-7.8)

Example 12

1,4-bis(3-propargyloxy-2-glycidyloxypropyloxy)-butane

15

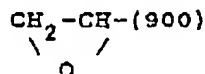
Epoxy equivalent : 165

Yield : 77.2 %

CH=C-(3300, 2100)

-CH₂-(2850)

20



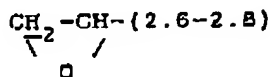
25

H-NMR (ppm) :

-CH₂-(1.62)

CH=C-(2.44)

30



35

Example 13

1,6-Bis(3-propargyloxy-2-glycidyloxypropyloxy)-hexane

40 Epoxy equivalent : 188

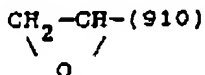
Yield : 80.0 %

IR (cm⁻¹) :

CH=C-(3300, 2100)

-CH₂-(2850)

45



50

H-NMR (ppm)

-CH₂-(1.62)

Ph-H(6.6-7.8)

55 Example 14

2,2-Bis[4-(3-propargyloxy-2-glycidyloxypropyloxy)-3,5-dibromophenyl]propane

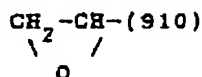
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Epoxy equivalent : 450

Yield : 88.1 %

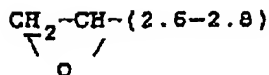
IR (cm⁻¹) :

CH=C-(3300, 2100)



H-NMR (ppm) :

CH=C-(2.44)



Ph-H(6.6-7.8)

Example 15

2,2-Bis[4-(3-propargyloxy-2-glycidyloxypropyloxy)-phenyl]-1,1,1,3,3,3-hexafluoropropane

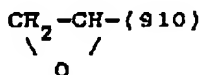
Epoxy equivalent : 345

Yield : 91.0 %

IR (cm⁻¹) :

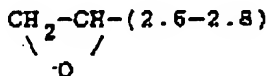
CH=C-(3300, 2100)

-PF-(1600, 1500)



H-NMR (ppm) :

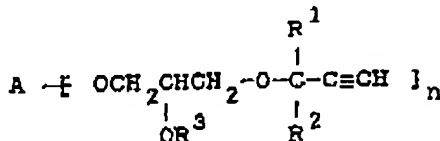
CH=C-(2.44)



Ph-H(6.6-7.8)

Claims

1. A compound of the formula:

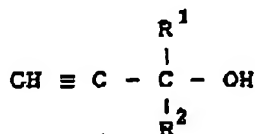


wherein A is the backbone residue of a glycidyl ether or ester type epoxy resin with removal of the

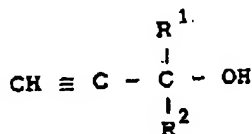
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terminal glycidyloxy groups; R¹ and R² are independently a hydrogen atom or C₁-C₁₂ alkyl; R³ is a hydrogen atom or glycidyl group; and n is an integer of greater than 1.

- 2 The compound as claimed in Claim 1, wherein R³ is a hydrogen atom, and wherein R¹ and R² are independently a hydrogen atom or C₁-C₄ alkyl.
- 3 The compound as claimed in claim 1, wherein R³ is a glycidyl group, and wherein R¹ and R² are independently a hydrogen atom or C₁-C₄ alkyl.
- 4 The compound as claimed in claim 2 or 3, wherein said residue A is derived from a bisphenol epoxy resin, a novolac epoxy resin, a glycol-diglycidyl ether epoxy resin, or a dicarboxylic acid-diglycidyl ester epoxy resin.
- 5 A method of modifying an epoxy resin having a plurality of terminal glycidyloxy groups which comprises reacting said epoxy resin with an acetylenic alcohol of the formula:



- wherein R¹ and R² are independently a hydrogen atom or C₁-C₁₂ alkyl.
- 6 The method as claimed in Claim 5, wherein the reaction is carried out in the presence of a basic catalyst.
- 7 A method of modifying an epoxy resin having a plurality of terminal glycidyloxy groups which comprises the steps of:
 - (a) reacting said epoxy resin with an acetylenic alcohol of the formula:



- wherein R¹ and R² are independently a hydrogen atom or C₁-C₁₂ alkyl;
- (b) reacting the product of step (a) with epichlorohydrine or glycerol-1,3-dichlorohydrine; and
- (c) reacting the product of step (b) with an alkali.
- 8 The method as claimed in Claim 7, wherein said step (b) is carried out in the presence of a Lewis acid catalyst followed by said step (c).
- 9 The method as claimed in claim 7 or 8, wherein said step (b) and said step (c) are carried out simultaneously using an excess of epichlorohydrine in the presence of a phase transfer catalyst, a tertiary amine or a quaternary ammonium hydroxide together with said alkali.
- 10 The method as claimed in anyone of Claims 5 to 9, wherein R¹ and R² are independently a hydrogen atom or C₁-C₄ alkyl.
- 11 The method as claimed in anyone of Claims 5 to 10 wherein said epoxy resin is a bisphenol epoxy resin, a glycol-diglycidyl ether epoxy resin, a dicarboxylic acid-diglycidyl ester epoxy resin, or a novolac epoxy resin.

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